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A new sample cell design for studying solid-matrix room-temperature phosphorescence moisture quenching

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Abstract

A new sample chamber was developed that can be used in the measurement of the effects of moisture on the room-temperature solid-matrix phosphorescence of phosphors adsorbed onto filter paper. The sample chamber consists of a sealed quartz cell that contains a special teflon sample holder. Sulfuric acid solutions in the quartz cell determine the percentage relative humidity in the cell and also determine the amount of moisture adsorbed onto the filter paper. The new sample chamber is much easier to use than a flowing nitrogen gas system. Results from both systems are compared with respect to ease of use and the amount of moisture adsorbed onto the filter paper.

1. Introduction

Solid-matrix room-temperature luminescence is a very useful analytical method for the trace analysis of organic compounds. The adsorption of organic molecules onto dry filter paper can reduce the non-radiative decay of a phosphor from the triplet state [1,2]. Solid-matrix room-temperature phosphorescence (SMRTP) and fluorescence (SMRTF) give greater quantum yields, in many cases, than the corresponding solution at low temperature [3]. In general, hydrogen-bonding interactions between the filter paper and the lumiphor is one of the main mechanisms responsible for the strong luminescence observed at room temperature [4]. The rigid environment provided by the filter paper reduces non-radiative transitions of the excited molecules and enhances luminescence.

Nissan [5] pointed out that the strength and number of hydrogen bonds in hydrogen-bond dominated solids, as measured by Young's modulus, decreases drastically upon the adsorption of moisture. The decrease in modulus is directly related to two regions of hydrogen-bond dissociation in paper [6]. The first region extends from zero moisture content to a point where a BET monomolecular layer of moisture has been established in the filter paper. The weight fraction of moisture at such monolayer coverage is designated as W_M. Within this region, only a single hydrogen bond is broken upon the adsorption of a water molecule. After the moisture content of the solid matrix exceeds W_M, cooperative hydrogen-bond dissociation dominates. In this region, groups of hydrogen bonds dissociate upon the adsorption of a single water molecule. Consequently, a more drastic decrease in the rigidity of the solid matrix is observed.

Schulman and Parker [7] presented evidence to indicate that the adsorption of moisture by filter paper permitted oxygen to penetrate the paper more efficiently. Citta and Hurtubise [8] reported that the SMRTP intensity of model aromatic compounds adsorbed onto filter paper decreased dramatically in the presence of humid nitrogen gas. In the presence of humid oxygen gas of 75% relative humidity (% RH), the SMRTP of the model compound they in-

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vestigated was completely quenched. Purdy and Hurtubise [9] observed that SMRTP lifetimes of model compounds were comparatively insensitive to moisture in nitrogen gas. The quenching of SMRTP was primarily a result of diminished filter paper matrix rigidity [9]. The moisture quenching of SMRTP for phosphors on filter paper was thus referred to as "matrix quenching" in contrast to the conventional static quenching in solution [9]. Chen et al. [10] introduced an equation that describes the changes in the SMRTP intensity as a function of SMRTP lifetime ratios and an exponential expression that included the weight percent of adsorbed moisture. Further, Chen and Hurtubise [11] introduced a model for the moisture quenching of SMRTP via the decrease in the Young's modulus of filter paper.

In previous studies of solid-matrix moisture quenching, moisture was introduced into the sample compartment of the luminescence spectrometer containing the filter paper sample via a flow of humid gas [8–11]. The amount of moisture in the flowing gas was determined by the flow rate of the gas through a series of sulfuric acid solutions [12]. In this work, a much simpler system was developed to obtain constant humidity in a sample chamber that contained the filter paper sample. This new sample chamber consists of a quartz cell and a teflon filter paper sample holder. Sulfuric acid solutions were added to the cell to create a humid environment surrounding the sample holder. It can be placed inside the sample compartment of a luminescence spectrometer, which eliminates the need to flow humidified nitrogen gas into the cell compartment.

2. Experimental

2.1. Apparatus

Intensity and lifetime measurements were obtained with a Fluorolog 2 + 2 spectrofluorometer (Spex Industries, Edison, NJ) interfaced with a Spex Datamate computer and the Spex 1934C phosphorimeter accessory. The excitation source was a 50 W programmable pulsed lamp. A cooled Hamamatsu R928 photomultiplier tube was employed. The % RH in the sample compartment of the spectrofluorometer and in the procedure used to obtain adsorption isotherms was measured with a Vaisala HMI 31 hygrometer (Vaisala, Helsinki, Finland).

2.2. Reagent and chemicals

Absolute methanol (Baker, HPLC grade) was mixed with water (Baker, HPLC grade) in a 1:1 ratio. Thallium acetate (Aldrich, 99.99%) and glacial acetic acid (ACS Reagent grade, Fisher Scientific) were added to the above solvent to give 0.5 M thallium acetate and 0.3 M acetic acid. Benzo[*a*]pyrene-*r*-7,*t*-8,9,*c*-10-tetrahydrotet-rol (tetrol I-1) was used as the model phosphor (Midwest Research Institute, Kansas City, MO), The tetrol solution was prepared by directly dissolving a weighed amount of tetrol in the thallium acetate solution as described previously [13]. The concentration of the tetrol solution was 40 ng μl^{-1}. Sulfuric acid (ACS reagent) was diluted in distilled water to various concentrations and stored in stopped bottles [12].

2.3. Materials

Whatman No. 1 filter paper (Whatman Co., Clifton, NJ) was developed three times in absolute methanol, dried at 110 °C for 30 min and stored in a desiccator. Small circular disks of filter paper that were 0.4 cm in diameter were obtained from the developed filter paper sheet using a commercial paper punch. A teflon sampler holder and a delrin sample holder were custom made to hold the filter paper samples (Fig. 1). A quartz cell (Wilmad Co., Buena, NJ) was used as the sample chamber to contain the teflon sample holder. Compressed nitrogen gas (US Welding, Golden, CO) was filtered through an oxygen trap (Oxyclear, Oakland, CA) and Drierite (W.A. Hammond Drierite Company, Xenia, OH). Chemical resistant Duraseal film (Diversified Biotech, Boston, MA) was used to seal the top of the 1 cm quartz cell. This film allows only 0.00807 $cm^3\ cm^{-2}\ h^{-1}$ of O_2 and 0.646 $\mu g\ cm^{-2}\ h^{-1}$ of H_2O to penetrate when used as described. An analytical balance was placed inside an Atomsbag (Aldrich) for the measurement of the weight increase of filter paper samples upon moisture adsorption in obtaining adsorption isotherms [10].

3. Experimental designs and procedures

3.1. Adsorption isotherm

An adsorption isotherm for water was obtained for thallium acetate treated paper as

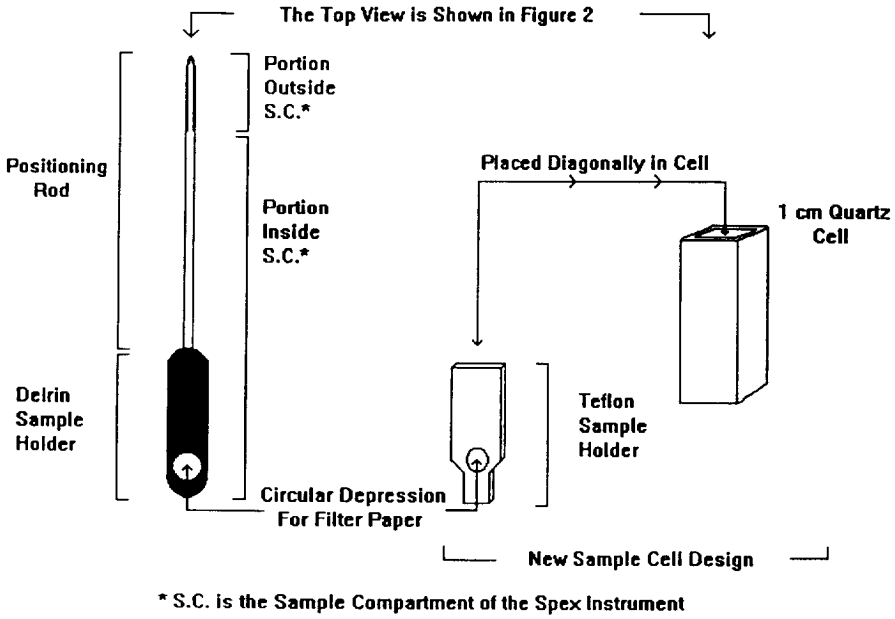

Fig. 1. Delrin and teflon sample holders.

described by Chen et al. [10]. Thallium acetate treated filter paper samples were suspended above sulfuric acid solutions of various concentrations for 45 min in stopped plastic bottles. The filter papers were weighed before and after this period of time. The adsorption isotherm was constructed by plotting the weight gained due to moisture adsorption against the % RH in the bottles. The % RH in the bottle was determined by the concentration of sulfuric acid, and the wt% of moisture at monolayer coverage (W_M) of thallium acetate treated filter paper was calculated using the BET method [14]. The data are given in Table 1.

The SMRTP quenching of I-1 was then determined in relation to the moisture content of the filter paper at various % RH. In general, the SMRTP intensities and phosphorescence decay curves were measured before and after the filter paper had acquired moisture. Moisture was introduced onto the filter paper via either a flow of humid nitrogen gas, or by suspending the filter paper sample above a solution of sulfuric acid in a sealed 1 cm quartz cell sample chamber. In both designs, filter paper samples were fitted into the sample holder. The sample holder was then placed in a sample chamber in which constant % RH was established. This is described in more detail below.

3.2. SMRTP quenching with flowing humid nitrogen gas

A delrin sample holder (see Fig. 1) was used to hold the filter paper samples. As indicated in the Figure, a positioning rod was attached to the upper part of the sample holder. The sample holder was placed on a stage inside the sample compartment of the spectrofluorometer.

Table 1
Adsorption isotherm data for thallium acetate treated whatman No. 1 filter paper

% RH	Moisture (wt%)
0	0.00
10	1.07
20	2.12
30	2.97
40	3.63
50	4.52
60	5.13
70	7.09
80	8.14
90	10.23
100	16.00

Each data point is the average of at least five trials. The standard deviation associated with each data point is less than 5%.

The linear region between 10 and 50% RH was used to calculate monolayer coverage, W_M. The calculated value of W_M was 2.47 wt% moisture. The linear correlation coefficient was 0.999 for the region from 10 to 50% RH.

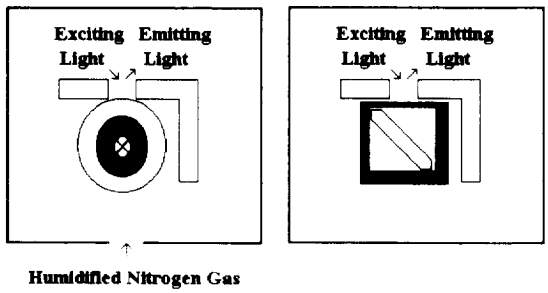

Fig. 2. Top view of sample holders in the cell compartment.

Fig. 2 illustrates the sample compartment of the instrument viewed from the top. The stage is indicated as a clear circle (left) and dark square (right) around the sample holders in Fig. 2. The upper 3 cm of the positioning rod was outside the sample compartment, so that the rotational orientation of the sample holder could be manipulated to obtain the maximum SMRTP intensity. The design on the left in Fig. 2 was used for flowing humid nitrogen gas. Compressed nitrogen gas was passed into the sample compartment via two paths. The nitrogen gas which came in via path (1) contained no moisture and provided 0% RH inside the sample chamber. The nitrogen gas which came in via path (2) was filtered through an oxygen trap and a set of three water bottles. Each water bottle contained approximately 500 ml of distilled water. The amount of moisture brought into the sample compartment via path (2) was determined by the flow rate of nitrogen gas. The %RH inside the sample chamber was constantly monitored by a digital hygrometer. It could be altered by adjusting the flow of gas through either path (1) or path (2).

One microliter of blank solvent was spotted on the surface of a filter paper sample which was on top of four other pieces of filter paper in the circular depression of the delrin sample holder (Fig. 1). The entire sample holder was dried in a oven at 110 °C for 30 min. It was then cooled at room temperature for 5 min under dry nitrogen gas inside the sample compartment. Both the blank and the sample were protected from the excitation light prior to the measurement step. The steady-state intensity of the blank filter paper was measured before the SMRTP decay curve of the blank filter paper was recorded. Dry nitrogen gas was continuously passed into the sample compartment throughout the measuring period. After obtaining SMRTP data under dry conditions, humid nitrogen gas from path (2) was directed into the sample compartment. Dry nitrogen gas inside the sample chamber was quickly displaced by the humid nitrogen gas. A fixed % RH was established inside the sample chamber within 20 min. The SMRTP intensity or phosphorescence decay curve of the humid blank filter paper sample was measured 45 min after a constant % RH inside the sample chamber was established. After blank measurement, the delrin sample holder was removed from the sample compartment and dried again at 110°C for 30 min. One-microliter aliquots of tetrol I-1 solution were transferred onto the top surface layer of the filter paper samples. After drying (30 min at 110 °C and then 5 min under dry nitrogen gas at room temperature), the steady-state SMRTP intensity and phosphorescence decay curve of I-1 on filter paper were measured. Mositure was then introduced again, and the SMRTP intensity and phosphorescence decay curve were obtained under humid conditions. The SMRTP intensity and phosphorescence decay curve from the blank filter paper samples were subtracted from the corresponding SMRTP intensity and phosphorescence decay curve of tetrol I-1 on dry and humid filter paper samples. The phosphorescence lifetimes of I-1 were calculated for dry and humid filter paper samples and are presented in Table 2 with respect to the moisture content of the filter paper.

3.3. SMRTP quenching within a Quartz cell sample chamber

A teflon sample holder was custom made to hold the filter paper samples (Fig. 1). A 1 cm quartz cell was used to hold the teflon sample holder. It was sealed with a piece of Duraseal film and fitted snugly on a metal stage inside the sample compartment of the spectrofluorometer (Fig. 2). The teflon sample holder containing the blank filter paper samples was dried under identical conditions to the delrin sample holder. It was transferred to the sample compartment of the spectrofluorometer and placed diagonally into a quartz sample cell (Fig. 1). Dry nitrogen gas was directed into the quartz sample cell via a glass pipette for 5 min before it was sealed with a square piece of airtight Duraseal film. The SMRTP intensity and phosphorescence decay curves of the blank filter paper samples were recorded under the identical instrumental conditions as the flowing nitrogen gas system. After the RTP data on dry filter paper sample was recorded, the

Table 2
τ_0/τ and P_0/P values for tetrol I-1 with flowing nitrogen gas and a quartz cell system

Moisture (wt%)	Flowing nitrogen gas [a]		Within quartz cell	
	τ_0/τ	P_0/P	τ_0/τ	P_0/P
0.00	1.00	1.00	1.00	1.00
1.42	1.12	1.05	1.05	1.08
1.87			1.07	–
2.12	1.20	1.38	1.10	1.17
2.97	1.22	1.78	1.26	1.27
3.63	1.24	1.98	1.27	2.54
4.52	1.17	2.63	1.38	4.37
5.38			1.52	–
5.57			1.60	–
7.09	1.17	3.80	1.77	9.66
7.50			1.90	–

[a] The τ_0/τ and P_0/P data were taken from Ref. [10].

Duraseal film was removed and 0.6 ml of a sulfuric acid solution was added to the quartz sample cell. A gentle stream of dry nitrogen gas was continuously passed into the quartz sample cell at 0.5 psi during the addition of sulfuric acid solution. The quartz sample cell was sealed again with a fresh piece of Duraseal film. The SMRTP intensity and decay curve of blank filter paper sample were recorded again after 45 min. After the measurements, the teflon sample holder was removed from the quartz cell and dried at 110 °C for 30 min. Sulfuric acid solution inside the quartz sample cell was discarded and the cell was rinsed with soap, nitric acid, tap water, distilled water and distilled ethanol, before being placed back onto the metal stage in the sample compartment. After drying, the teflon sample holder was cooled under dry nitrogen gas for 5 min at room temperature. One microliter of tetrol I-1 solution was spotted onto the top filter paper sample. The entire sample holder was dried again at 110 °C for 30 min. It was placed back into the quartz sample cell and cooled under dry nitrogen gas. The SMRTP intensity and phosphorescence decay curve of the tetrol on dry and humidified filter paper samples were recorded in the same fashion as the blank filter paper samples. The blank SMRTP intensity and phosphorescence decay curve data were subtracted from the corresponding sample data for I-1. The results are presented in Table 2.

3.4. Measuring the steady state SMRTP intensity and lifetime

The steady state SMRTP intensity of the tetrol was measured by setting both the excitation and emission monochromators at appropriate wavelengths ($\lambda_{ex} = 345$ nm and $\lambda_{em} = 608$ nm). The initial delay was set at 0.1 ms, the gatetime (specified as "window" in Spex) was set at 5 ms, and the average intensity was obtained from 20 intensity values. The SMRTP decay curves of the filter paper and tetrol I-1 were also recorded at the excitation and emission wavelengths mentioned above. A phosphorescence lifetime program was loaded into the Datamate computer to obtain the phosphorescence decay curve. The phosphorescence decay curves obtained from filter paper samples with various moisture contents were all measured with 0.03 ms delay, 5 ms gatetime, and five flashes per data point. A time period of 0.07 ms was allowed between each flash, with 0.1 ms between consecutive data points. A total of 200 points was collected in constructing the phosphorescence decay curve. After subtracting the blank decay curve, the data for the phosphorescence decay curve from 0.03 to 12.75 ms were used in a linear regression program. The SMRTP lifetimes of the tetrol samples were calculated from the slope of the regression line.

4. Results and discussion

The weight percent (wt%) moisture values obtained on thallium acetate treated filter paper samples at a given %RH are presented in Table 1. The moisture content of filter paper increased linearly between 5 and 50% RH, and then more drastically above 70% RH. The linear correlation coefficient between 5 and 50%

RH was over 0.999. Using the linear portion between 5 and 50% RH, the monolayer coverage of water (W_M) was calcualted to be 2.47% using the BET method. This corresponds to approximately 24% RH. The point at which W_M occurs is important because, as discussed in the Introduction, it separates two regions of hydrogen bond dissociation.

Table 2 lists the ratios of SMRTP intensities (P_0/P) and lifetimes (τ_0/τ) in relation to various percentages of moisture content in the filter paper. P_0 represents the SMRTP intensity on dry filter paper and P represents the corresponding intensity with moisture. Similarly, the term τ_0 is the SMRTP lifetime without moisture, and τ is the corresponding lifetime with moisture present. Each data point in Tables 1 and 2 represents the average of at least two trails.

As indicated in Table 2, the SMRTP intensity of I-1 was not affected much by moisture before W_M. The τ_0/τ values also changed little for the flowing nitrogen gas system. After the wt% of water had reached about 2.0%, the P_0/P values changed more rapidly with the flowing nitrogen gas system compared to the τ_0/τ values with this system. The τ_0/τ results from the quartz cell showed a similar trend compared to the flowing nitrogen gas system up to approximately 3.6 wt% water. After about 4.5 wt% water was adsorbed, the τ_0/τ values became larger compared to the τ_0/τ values obtained from the flowing nitrogen gas system. The P_0/P ratios with the quartz cell system were considerably larger after about 4.5 wt% water, compared to the P_0/P ratios from the flowing nitrogen gas system. Fig. 3 illustrates the data in Table 2 for both systems.

In general, the results from the two systems gave similar trends. The adsorption of moisture can be separated into two regions, as discussed by Chen et al. [10]. In the first region, which extends from 1 to about 2.5 wt% water, dynamic quenching dominates the entire quenching process. The intensity and lifetime ratios were about the same. In the second region, the P_0/P ratio increased much faster than the τ_0/τ ratios (Fig. 3). Fig. 3 clearly showed that identical quenching was not obtained for both systems over the entire wt% water range for the corresponding τ_0/τ and P_0/P ratios. This is most likely related to the fundamental differences between the two systems. With the flowing nitrogen gas system, the humidified nitrogen gas flows into and also exits the sample chamber. The nitrogen gas is constantly in motion, and thus moisture would not absorb as readily onto the filter paper as with a static system. The quartz cell sample chamber can be considered as a static system. As Fig. 3 shows, at greater than 3.5 wt% moisture, more water was adsorbed by the filter paper as indicated by the greater change in the P_0/P ratios with the quartz cell compared to the flowing system. This is a result of the moisture being in more intimate contact with the filter paper in the quartz cell. In the flowing system, the cell compartment is very large and the humidified nitrogen is readily dispersed compared to the closed 1 cm quartz cell. The results in Fig. 3 showed that the type of system used to study moisture adsorption on filter paper is important, and the results are influenced by the design of the system. Thus, it would be important to use the same system for a given set of experiments to acquire consistent results.

Another important consideration related to the results in Fig. 3 is that the wt% water adsorbed onto the filter paper was obtained by

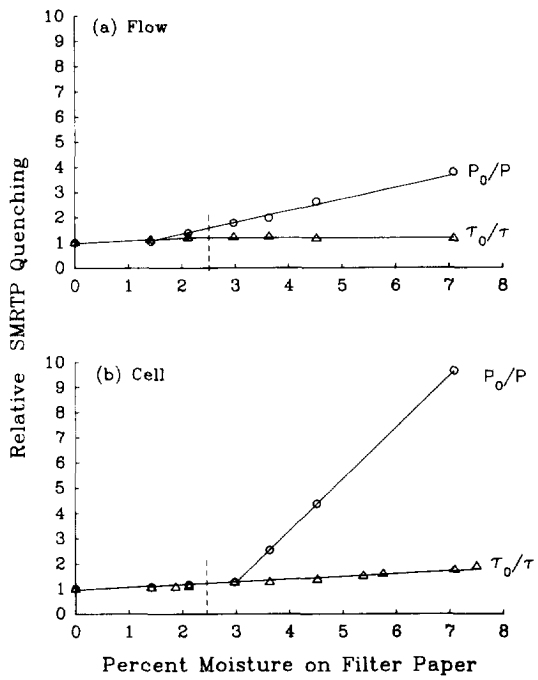

Fig. 3. SMRTP quenching of tetrol I-1(a) on Whatman No. 1 filter paper treated with thallium acetate-acetic acid solution under a flow of humid nitrogen gas (data from Ref. [10]), and (b) inside a sealed quartz sample cell. The ratio P_0/P refers to the phosphorescence intensity ratio, and the ratio τ_0/τ refers to the phosphorescence lifetime ratio. See text for additional details.

first suspending filter paper samples in bottles containing sulfuric acid solutions, and then weighing the samples in a humidity controlled environment. Most likely, the wt% moisture obtained under these conditions would be very similar to that in the quartz sample chamber. However, because all three systems (quartz cell, flowing system, and bottles with sulfuric acid) are not identical, the wt% moisture values in Table 1 would be proportional to the true wt% moisture adsorbed for the two systems investigated. This is indicated by the results in Fig. 3. The wt% moisture used in Figs. 3(a) and 3(b) is identical for both wt% moisture axes, but beyond 3.5 wt% moisture the P_0/P values for the two systems become considerably different.

The trends in τ_0/τ ratios obtained from the two systems are different. With the quartz cell, the τ_0/τ ratio gave an approximate linear relationship with wt% moisture. The τ_0/τ ratios for the flowing nitrogen gas system essentially reached a constant value above about 2.12 wt% water. Matrix quenching was more effective in the new sample chamber as indicated in Fig. 3 with the much greater slope of the P_0/P plot in the region beyond 3.0 wt% water for the quartz cell. Matrix quenching involves the participation of moist filter paper in the quenching process. This type of quenching has been discussed by Chen et al. [10]. The separation between the two regions of SMRTP quenching discussed was also better clarified using the new design. It occurred slightly beyond W_M at 3% moisture content (compare Figs. 3(a) and 3(b)). Using the new quartz cell design, the effects of a humid environment can be studied in the sample compartment of commercial luminescence instruments. In addition, the quartz sample cell can be transferred easily so that data can be obtained from instrument to instrument.

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